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DETERMINATION OF ORGANOLEAD COMPOUNDS IN INDUSTRIAL EFFLUENTS

M.J. Powell, Ijaz Ahmad, and Lynn Glassford, Ontario Ministry of the Environment, Laboratory Services Branch, 125 Resources Rd., Rexdale, Ontario M9W 5L1.

SUMMARY

Organolead compounds are used as "anti-knocking" agents in gasoline to increase the efficiency and longevity of high compression engines. The toxic affect of these compounds on humans is well known. Governments in North America have now restricted the use of these compounds in gasoline, however many other parts of the world such as Europe and Asia have not. In Ontario, these compounds are produced for export overseas.

The Ontario Ministry of The Environment has set guidelines for the amounts of organolead compounds in industrial effluents. The Ministry has developed a method for analyzing these compounds for regulation monitoring. This paper describes the development of this method, instrumental optimization, in-situ derivitization/extraction and quality control data.

INTRODUCTION

Despite the benefits of organolead as an octane enhancer and a valve seat lubricant, scientific research has demonstrated conclusively that negative health and detrimental environmental effects of lead far outweigh it's advantages as a gasoline additive. Acute lead poisoning has been reduced in North America because of the use of "unleaded gasolines". However, chronic exposure to low levels of lead in the environment still remains a serious concern. In the mid 1980's, governments in North America restricted the use of lead in gasoline. Farm and aviation fuel are the only known exceptions. Although organolead compounds are not being used locally in gasoline, they are still being produced for export overseas in Ontario. The municipal and industrial strategy for abatement (MISA) program incorporated by the Ontario Ministry of the Environment dictates that it is the responsibility of the industry or municipality to monitor and control, to provincial guidelines, the concentration of pollutants in their effluent. Regulation monitoring is conducted by the Ministry on a random basis to assure the company is conforming to the provincial guidelines. For this purpose, the Laboratory Services Branch has developed a method for analyzing organolead compounds in industrial effluent.

Methods available for the determination of alkyl lead compounds include spectrophotometric measurements of their dithizonates in chloroform at different wavelengths¹, and of their dialkyllead complexes with 4-(2-pyridylazo)resorcinol after conversion of the trialkyl lead to dialkyllead with iodine monochloride². These methods are lengthy and lack speciation.

Other methods include gas chromatography (GC) with an electron capture detector³, gas chromatography - microwave induced plasma - atomic emission detection (GC-MIP-AED)⁴, and gas chromatography - atomic absorption spectrophotometry (GC-AAS)⁵. All of these methods use an extraction of lead compounds from an aqueous solution after chelation with appropriate reagents. The combination of gas chromatography and atomic absorption spectrophotometry has proved to be an excellent technique for the determination of the above compounds because of its sensitivity and the ability to speciate and will be used for this method. The compounds to be analyzed are tetramethyl (Me₄Pb), tetraethyl (Et₄Pb), trimethyl (Me₃Pb), triethyl (Et₃Pb), dimethyl (Me₂Pb) and diethyl (Et₂Pb) lead.

EXPERIMENTAL

A Hewlett Packard 5890 Gas Chromatograph (GC) equipped with a Supelco megabore fused silica DB1 capillary column (30 m in length X 0.530 mm I.D. - 1.4 µm film thickness) was used for separation. The transfer line was constructed of 1/16" I.D. stainless steel tubing about 3 ft in length. The quantitation was performed by using a Perkin-Elmer 2380 atomic absorption spectrophotometer (A.A.) with a quartz furnace for atomization. The data was recorded on a Varian 7240 integrator.

The operating conditions for the GC were set at 150 degrees celsius for the injection port temperature and 0 - 200 degrees celsius for the oven temperature at programmed stages. The transfer line was heated to 70 degrees celsius with nitrogen carrier gas flowing through at 10 ml/min. The A.A. wavelength was set at 217.4 nm with a slit width of 0.7 nm. The quartz furnace was heated to 900 degrees celsius.

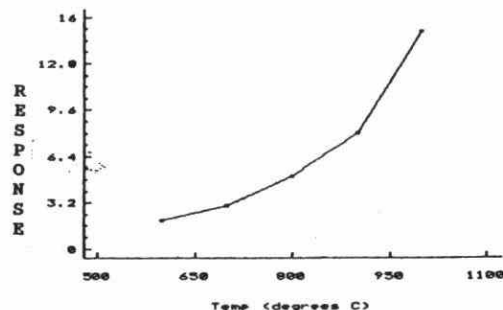
Sample Storage and Preparation

The samples were received in 1 litre amber glass bottles lined with teflon caps. They were stored at 4 degrees celsius and the analysis was performed within 2 weeks. The sample preparation involved removing a 10 - 11 ml sample and displacing it with 10.0 ml of hexane. The bottle was capped and rotary tumbled for 30 min. The organic phase was separated, dried with anhydrous sodium sulphate and analyzed. The volume of the remaining sample was adjusted to 800 ml. Sodium chloride (50 g) and aqueous 0.5M sodium diethyldithiocarbamate (50 ml) were added to the sample. The solution was extracted with 2 X 50 ml hexane. It was rotary tumbled for 30 min with each extraction. The organic phase was separated and dried with sodium sulphate. Toluene (4 ml) was added to the extract and then it was concentrated to 3 - 4 mls. Butyl Grignard reagent (Aldrich, 1.9M in THF) at a volume of 0.5 ml was added, mixed and kept at room temperature for 10 min. The volume was adjusted to 5.0 ml with toluene. It was then cooled in an ice bath and washed with 4-5 ml of 0.5M sulphuric acid to destroy the excess Grignard reagent. A portion of the extract was dried with sodium sulphate and analyzed for trialkyl and dialkyl lead compounds.

RESULTS AND DISCUSSION

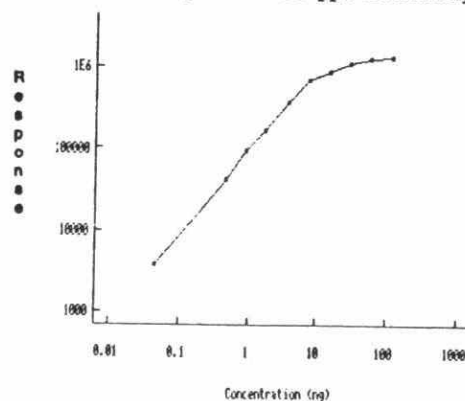
1. Instrument Optimization. The optimization of the instrumentation included injection port temperature, carrier gas flowrate, oven temperature, A.A. slit width, A.A. wavelength, furnace temperature, furnace alignment, hydrogen flowrate and transfer line temperature. The most critical parameter was furnace temperature. An optimum was not reached due to the thermal breakdown of the furnace winding. Consequently, optimum sensitivity is not achieved. More experimentation with a heavier gauge furnace wire will be conducted in the future. A compromise temperature of 900 degrees celsius was used. A response profile for several furnace temperatures is shown in FIG 1.

FIG 1. Profile - Response VS Furnace Temperature
50 ppb Tetraethyl Lead



2. Linear Dynamic Range. The linear dynamic range was determined to be approximately 3 orders of magnitude from the instrument detection limit. FIG 2. shows a response while varying concentrations of tetraethyl lead.

FIG 2. Concentration VS Response - 50 ppb Tetraethyl Lead



3. Quality Control Data.

Recovery studies were performed by spiking double distilled water samples at 20 and 50 ug/l. Eight replicates were spiked and analyzed and the data is given in Table 1 and Table 2. The method detection limits (MDL'S) were determined to be 0.5 to 2.0 ug/l and were calculated according to method development protocol⁴. The quality control data on dialkyl lead compounds was not available because of the lack of pure standards. Future attempts to synthesize purer standards will be conducted.

Table 1. Recovery Data @ 20 ug/l. n = 8 replicates

Parameter	Recovery(%)	%RSD	MDL(ug/l)
Me ₄ Pb	87 - 96	11	0.8
Et ₄ Pb	80 - 112	21	2.0
Me ₃ Pb	90 - 104	2	0.5
Et ₃ Pb	85 - 110	9	1.0

Table 2. Recovery Data @ 50 ug/l. n = 8 replicates

Parameter	Recovery(%)	%RSD	MDL(ug/l)
Me ₄ Pb	93 - 96	5	0.5
Et ₄ Pb	90 - 106	10	2.0
Me ₃ Pb	90 - 114	10	1.5
Et ₃ Pb	85 - 110	8	1.0

The method was successfully tested on an actual industrial effluent. The data obtained by standard addition in six industrial effluents was found to be within the limits reported in Table 1 and Table 2.

CONCLUSIONS

1. The instrumental optimization was performed. The furnace temperature of the A.A. was found to be the most critical parameter on sensitivity.
2. A method has been established for the analysis of tetra alkyl and tri alkyl lead compounds. Detection limits, linear dynamic range, precision and extraction efficiency data were within the MISA methods development protocol.
3. Work for the determination of di alkyl lead compounds is in progress.

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